Electrolytes and Interfaces for Stable High-Energy Na-Ion Batteries

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2020 DOE VTO Annual Merit Review

Project ID #bat429

June 1-4, 2020

Overview

Timeline

- Start date: Oct. 1, 2018
- End date: Sept. 30, 2021
- Percent complete: 53%

Budget

- Project funding
  - DOE share 100%
- Funding for FY19: $400K
- Funding for FY20: $430K

Barriers

- Short cycle life: Need functional electrolyte enabling stable electrolyte/electrode interface for long cycle life.
- High cost: Need low cost and sustainable anode and cathode material to enable electric vehicle (EV) battery cost < $100/kWh.

Partners

- Argonne National Laboratory
- Lawrence Berkeley National Laboratory

Relevance/Objectives

Impact

- Design and understand the electrolytes and electrolyte/electrode interface is critical to enable Na-ion batteries (NIBs) to be an alternative, low-cost battery solution for EV applications.

Objective

- Develop innovative electrolytes and fundamental understanding on the interface between the electrode and electrolyte for stable operation of high-energy NIBs.
  - Identify the correlation (electrolyte design rule) between the electrochemical performance of NIBs with the electrolyte/interface properties.
  - Enable long cycle life and safe operation of high-energy NIBs.
  - Increase the energy density of NIBs by developing high-capacity anode materials.

Milestones

Date	Milestone Name/Description	Status
Dec. 31, 2019	Optimize electrolyte composition for NIBs.	Completed
Mar. 30, 2020	Develop electrolyte additives to improve the stability of SEI on anode and CEI layer on cathode.	Completed
June 30, 2020	Develop compatible polymer separator (or polymer electrolyte) to stabilize long-term cycling and provide a stable/adequate interphase.	On track
Sept. 30, 2020	Apply the new electrolytes and additives in NIBs to improve its CE to be more than 99%.	On track

Approach

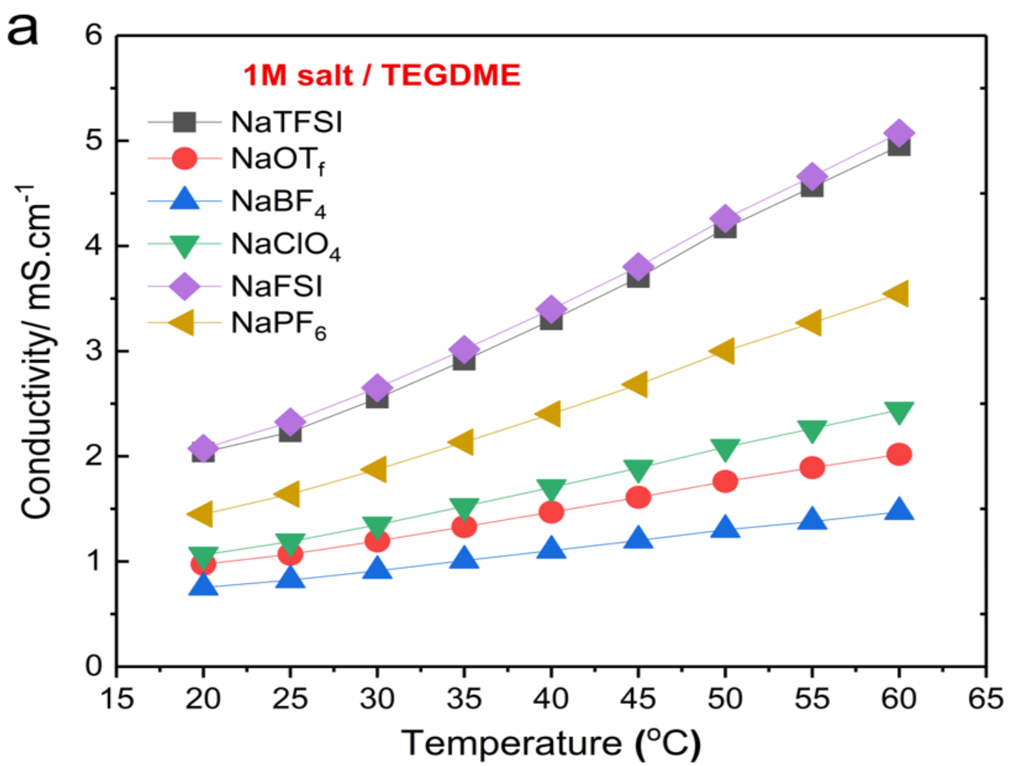
1. Develop ether-based electrolyte for stable Na metal and hard carbon anode.

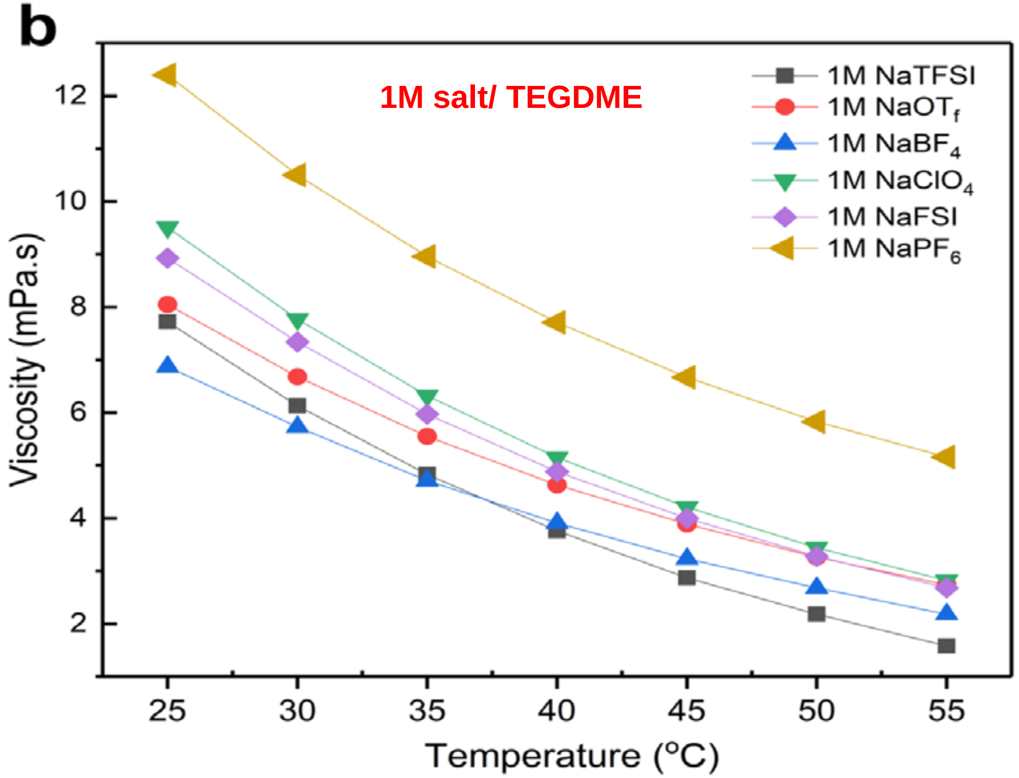
2. Identify the effects of salts and carbonate solvents on the performance of NIBs.

3. Develop phosphate-based localized high-concentration electrolytes (LHCE) to improve the performance of NIBs.

4. Develop high-capacity carbon anode.

Technical Accomplishments





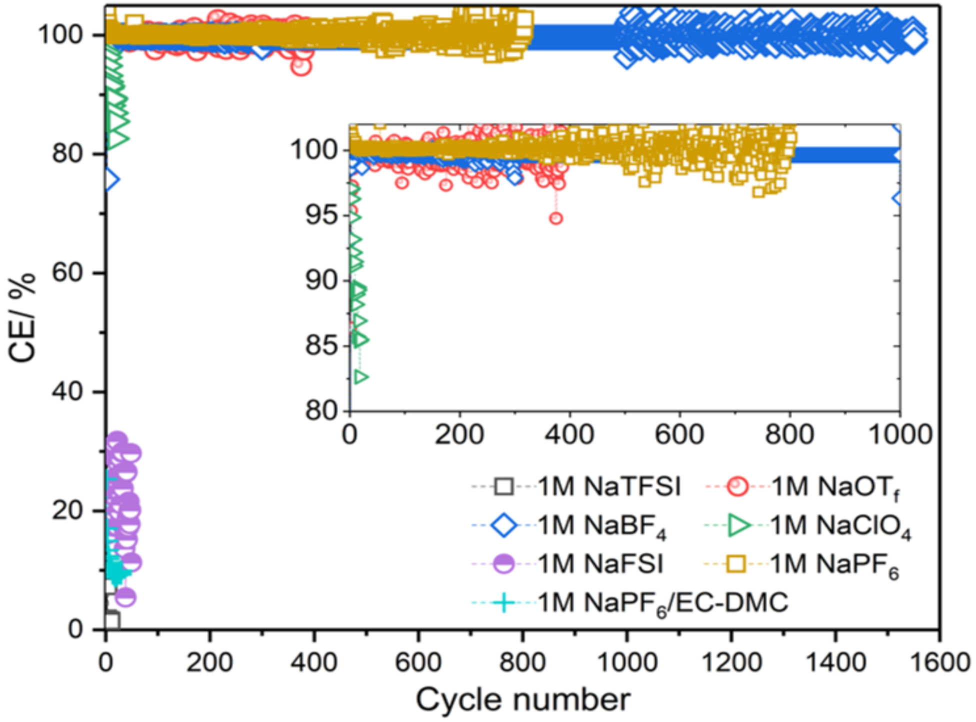
Salt dissociation order: NaFSI ~ NaTFSI > $NaPF_6$ > $NaClO_4$ > NaOTf > $NaBF_4$

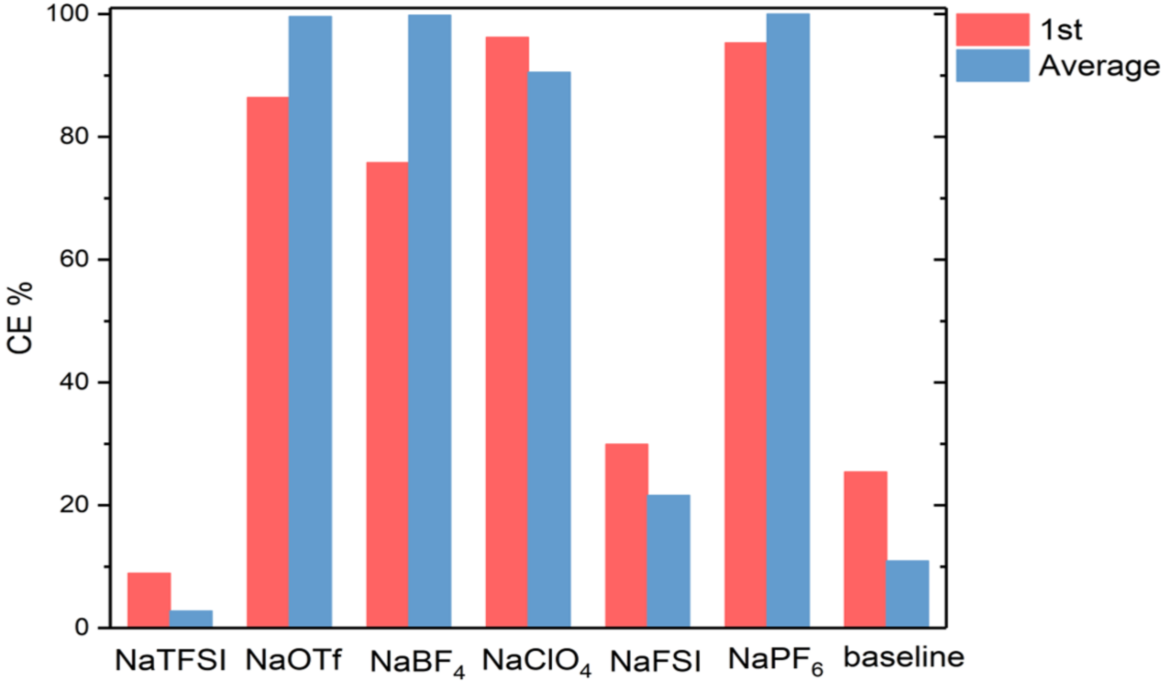
Le and Zhang et al., Advanced Functional Materials, 2020, 2001151

Technical Accomplishments

Stability of Na Metal Anode in Ether-based Electrolytes

Cu||Na cells; 0.5 mA cm^{-2}; 0.5 mAh cm^{-2}



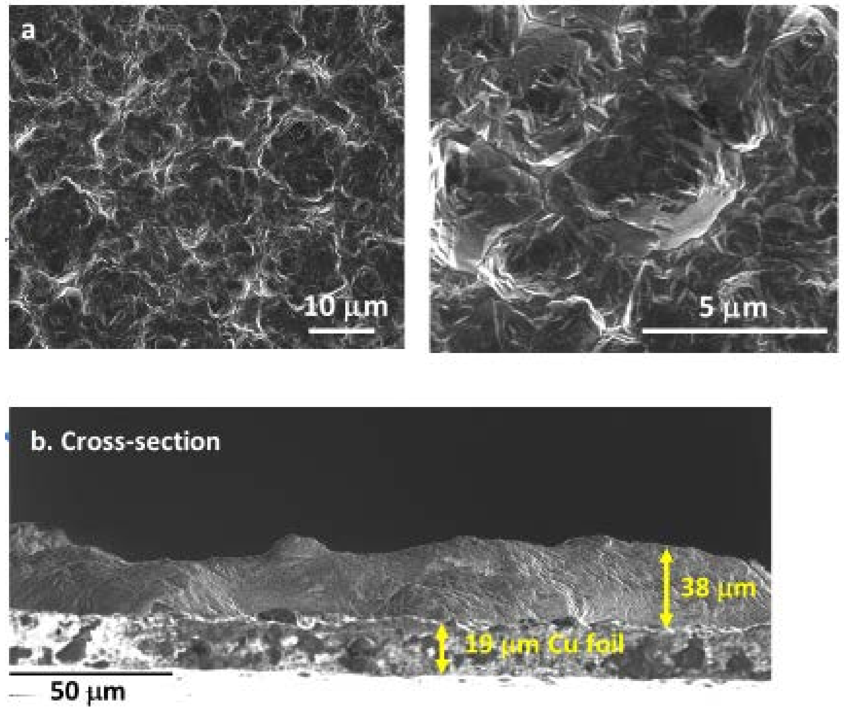


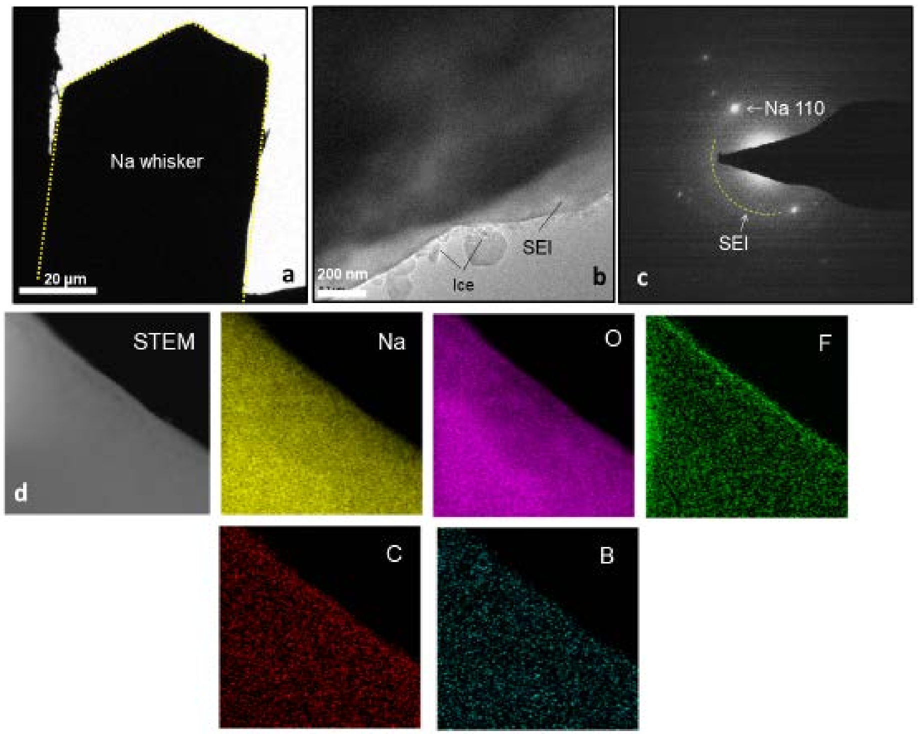
- Na anode exhibits an excellent CE (> 99.9%) when tested in Cu||Na cells.
- Cu||Na cells in $NaBF_4$/TEGDME demonstrated the best long-term cycling stability.

Le and Zhang et al., Advanced Functional Materials, 2020, 2001151

Technical Accomplishments

Morphology of Na and Compositions of SEI layers investigated by Cryo-TEM



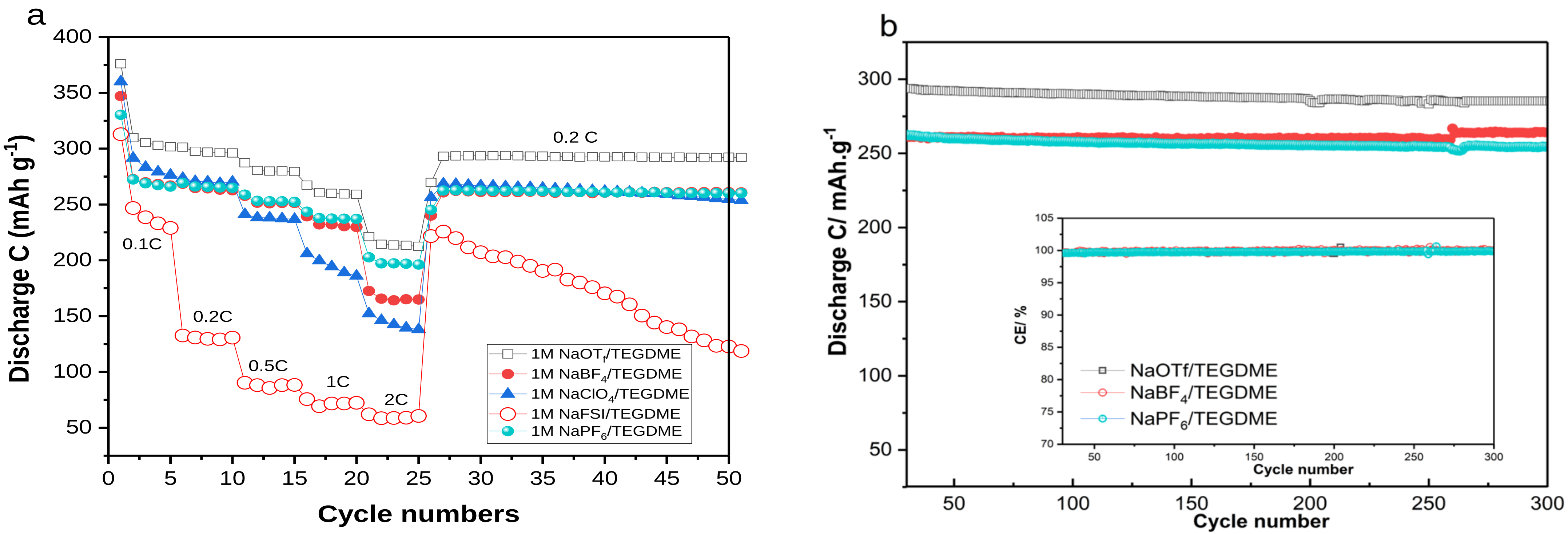


- 1 M $NaBF_4$/TEGDME electrolyte enables compact and granular Na particle deposition.
- SEI thickness is ~214 (+/- 15 nm) in a 1 M NaBF4/TEGDME electrolyte.
- SEI composition is rich in inorganic species (O, F, C, and Na).

Le and Zhang et al., Advanced Functional Materials, 2020, 2001151

Technical Accomplishments

Performance of Na||Hard Carbon Cells in Ether-based Electrolyte



Note: Na||HC half cells, HC electrode: HC:PVDF:CB=90:5:5, mass loading: 2–3 mg/cm^2

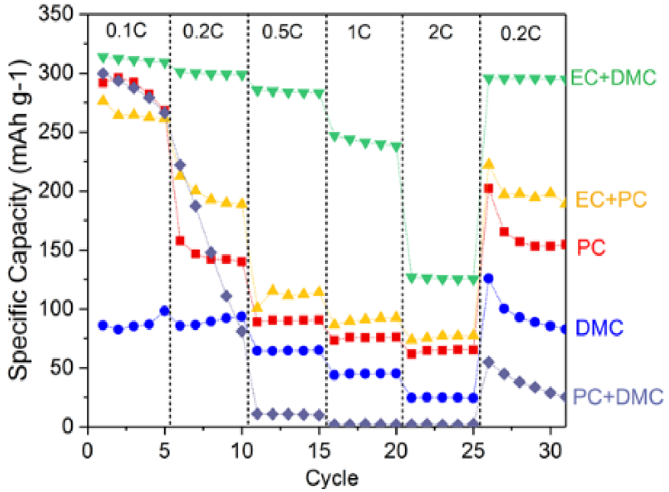
- Na||HC cells with NaOTf/TEGDME electrolyte exhibit a high capacity (293.2 mAh g^{-1} @ 0.2 C) and stable long-term cycling stability.
- The cells also demonstrate excellent high-rate performance (213 mAh g^{-1} @ 2 C).

Le and Zhang et al., Advanced Functional Materials, 2020, 2001151

Technical Accomplishments

2. Effects of the Salts and Carbonate Solvents on the Performance of Na||Hard Carbon Cells

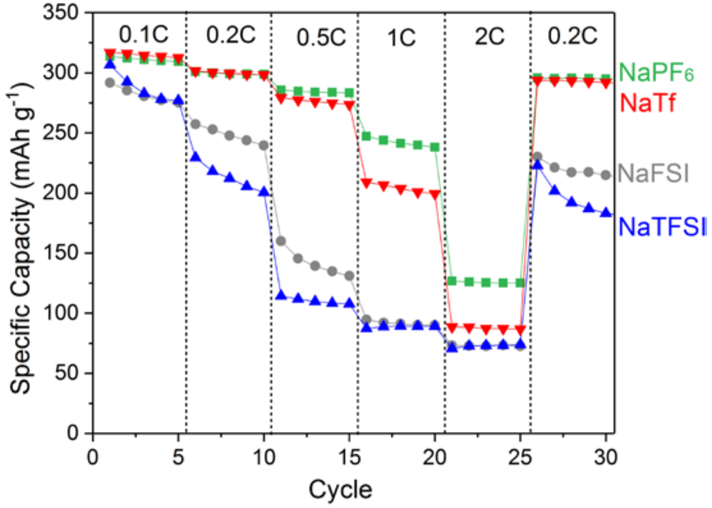
Solvent effect



1M $NaPF_6$ in different solvent

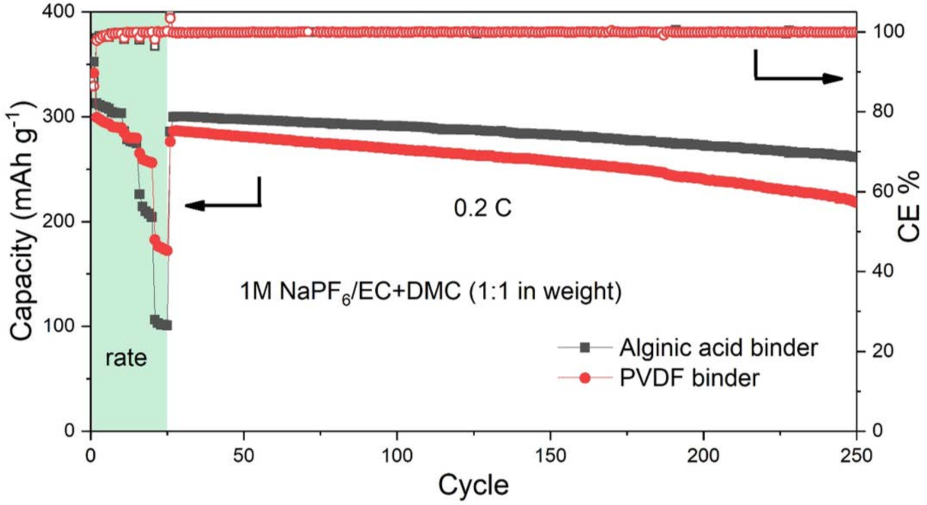
1:1 in weight for two solvents system

Salt effect



Different salts in EC/DMC (1:1 in weight)

Long cycling



Note: Na||HC Half cells

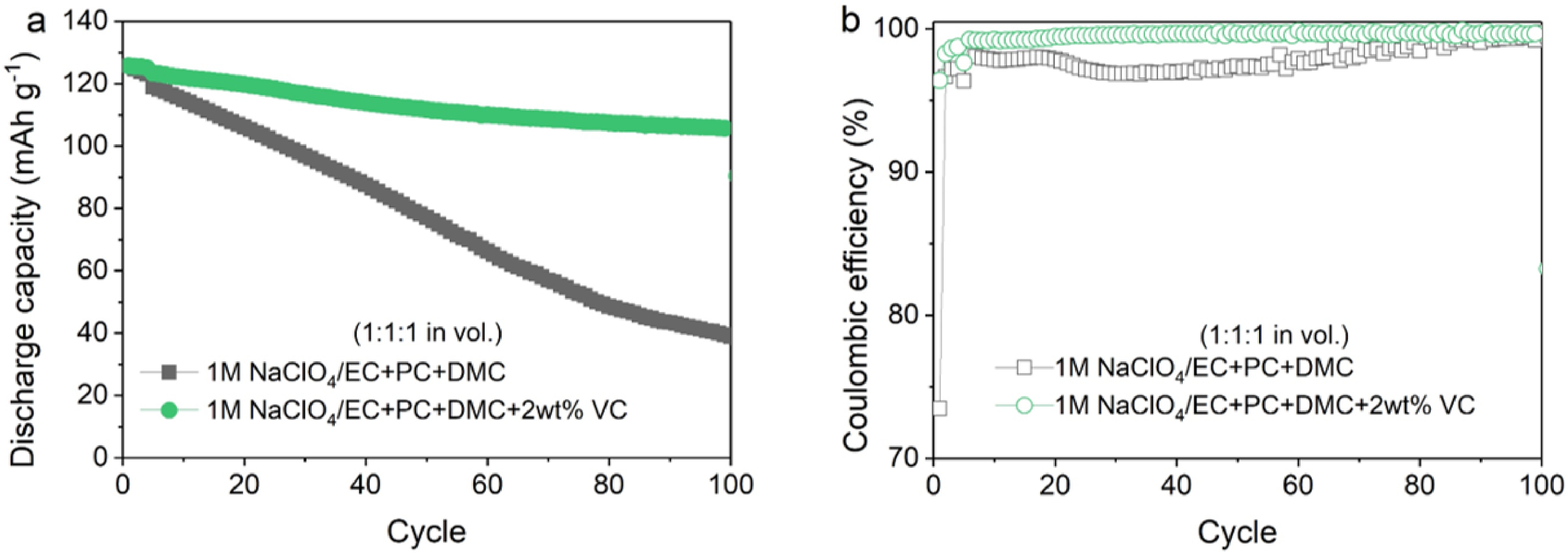
HC electrode: HC:PVDF:CB=90:5:5

mass loading: 2–3 mg/cm^2

- Na||HC cell with 1M $NaPF_6$/EC+DMC (1:1 in weight) exhibits best overall performance.
- Na||HC cell shows 87.71% ICE and 261 mAh g^{-1} reversible capacity after 250 cycles.

Technical Accomplishments

Effects of VC Additive on Cathode Performance



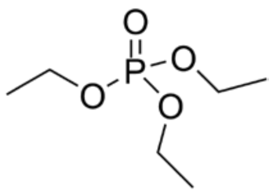
Note: Na ǁ O3-$NaCu_{1/9}Ni_{2/9}Fe_{1/3}Mn_{1/3}O_2$. Loading: ~14 mg/cm^2

2 wt% VC additive can further improve cathode stability and coulombic efficiency.

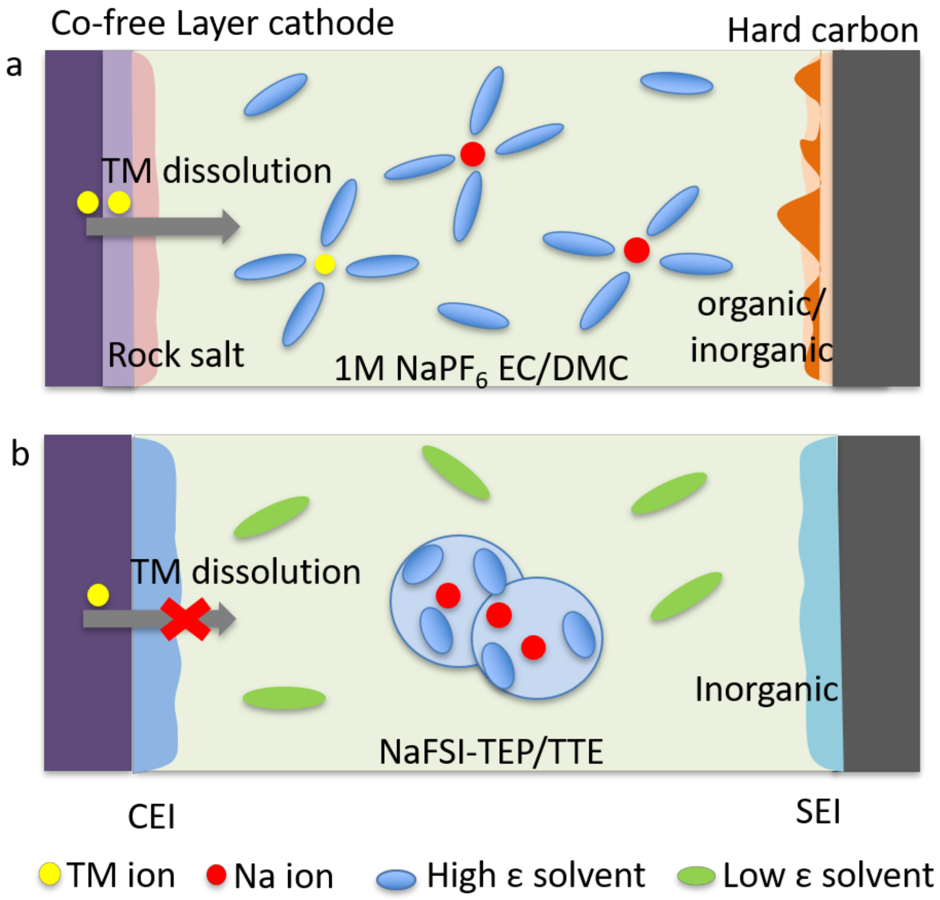
Technical Accomplishments

3. Phosphate-based Localized High-Concentration Electrolytes (LHCE) for NIBs

Triethyl phosphate
(TEP)

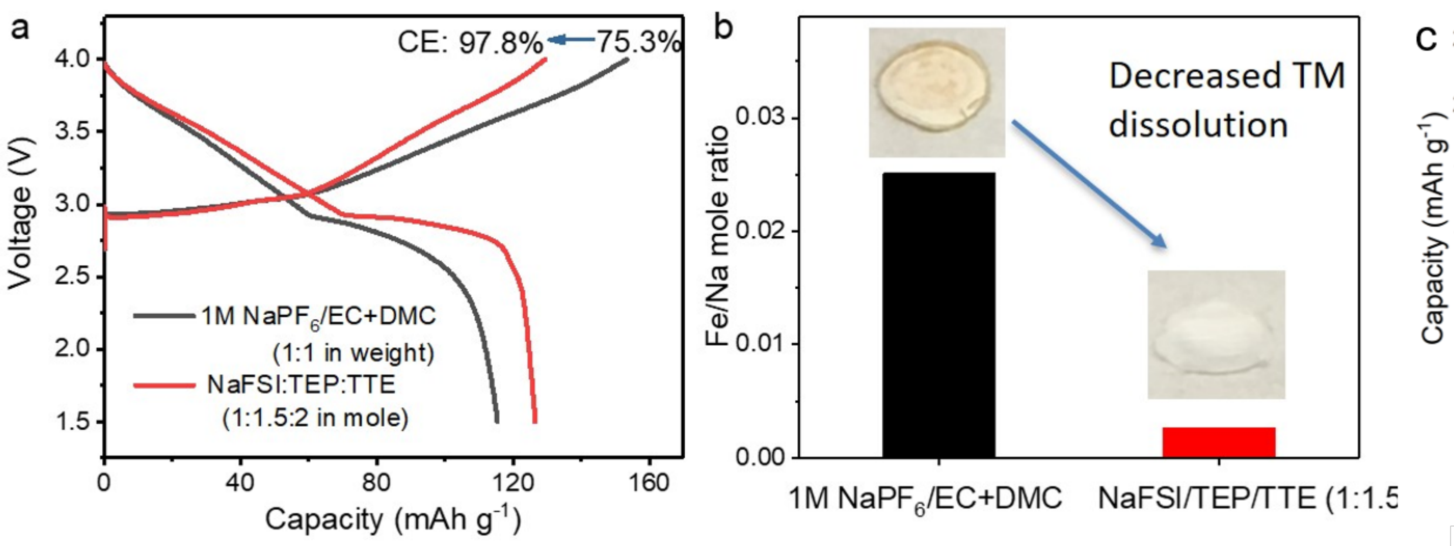


- ✓ High oxidization window
- ✓ High thermal stability
- ✓ **Nonflammable**



Technical Accomplishments

Phosphate-based LHCE for Cathode

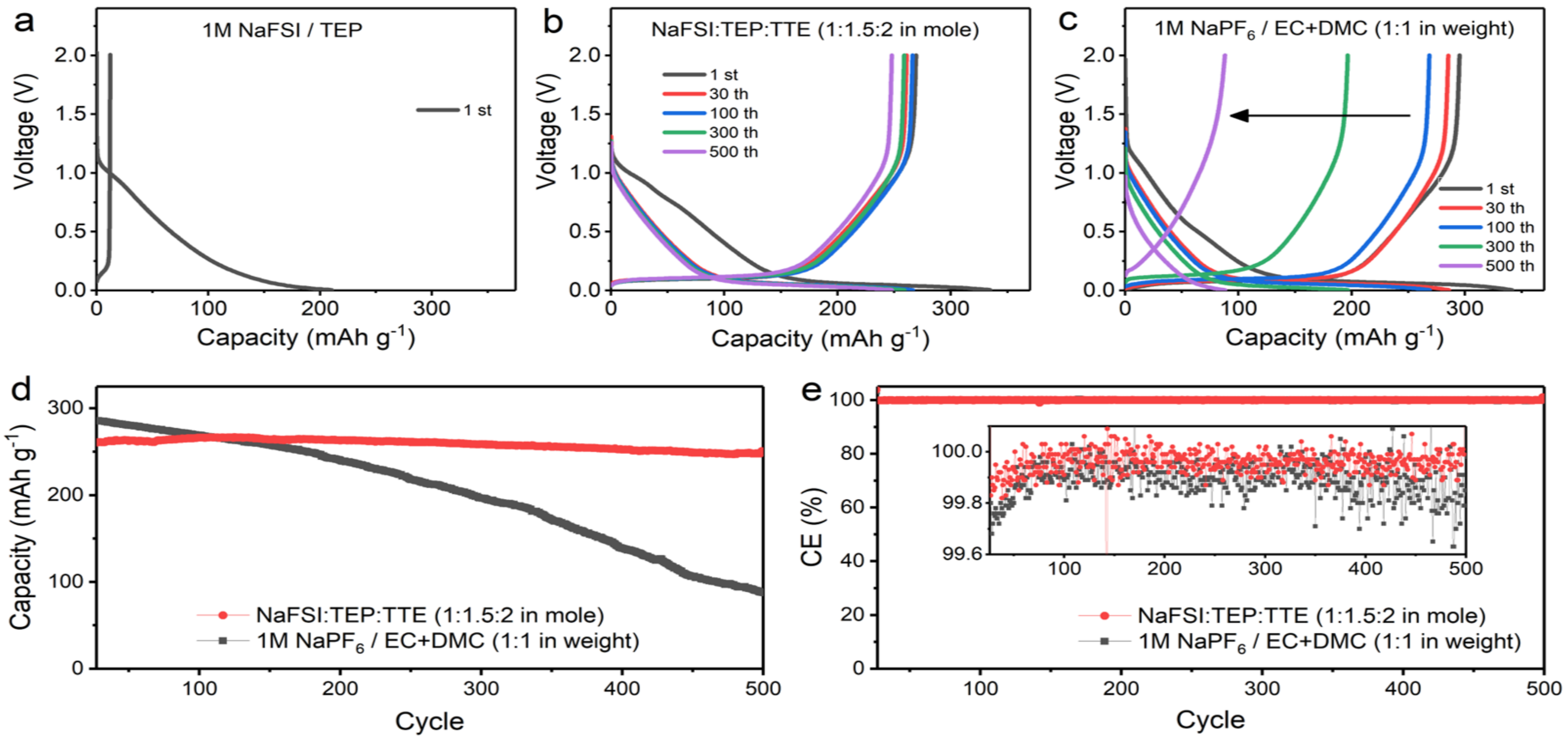


Note: Na ǁ O3-$NaCu_{1/9}Ni_{2/9}Fe_{1/3}Mn_{1/3}O_2$ half cell was used to evaluate for phosphate electrolyte. Loading: ~16 mg/cm^2

The TEP-based LHCE electrolyte greatly improved initial coulombic efficiency (from 75.3% to 97.8%). It also suppressed transition metal dissolution and improved capacity retention of half cells.

Technical Accomplishments

Stability of Phosphate Electrolyte in Na||HC Cells



Na||HC cell with phosphate based LHCE (NaFSI:TEP:TTE (1:1.5:2 in mole) demonstrates excellent capacity retention of 94.8% after 500 cycles (compared with 30.8% capacity retention in carbonate electrolyte).

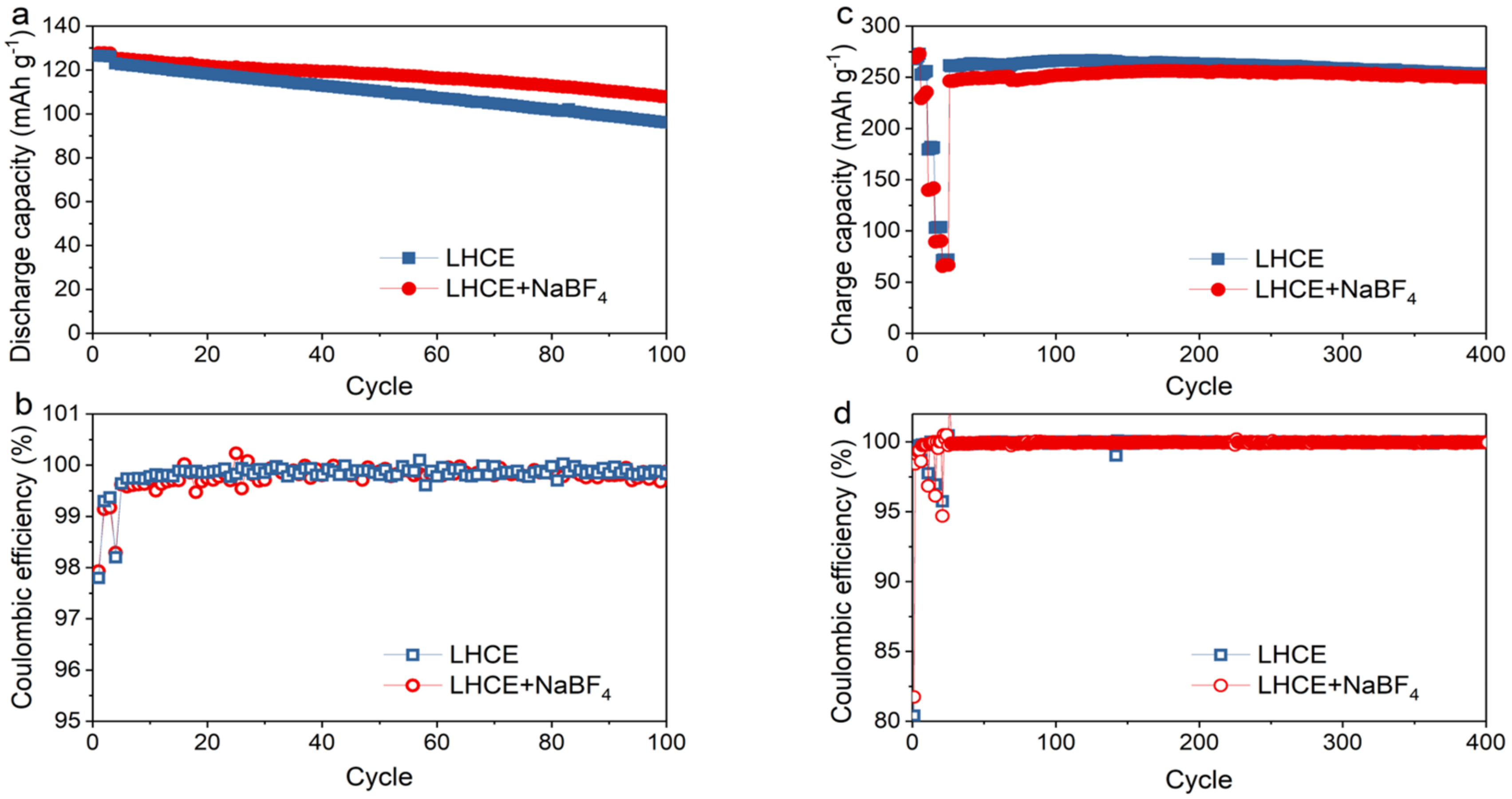
Note: Na ǁ hard carbon half cell. Loading: 2~3 mg/cm^2

Technical Accomplishments

Effects of $NaBF_4$ Additive in Phosphate Electrolyte

Cathode performance

Anode performance



Na ‖ O3-$NaCu_{1/9}Ni_{2/9}Fe_{1/3}Mn_{1/3}O_2$ half cell. Loading: ~16 mg/cm^2.

Na ‖ hard carbon half cell. Loading: 2~3 mg/cm^2.

LHCE: NaFSI:TEP:TTE (1:1.5:2 in molar).

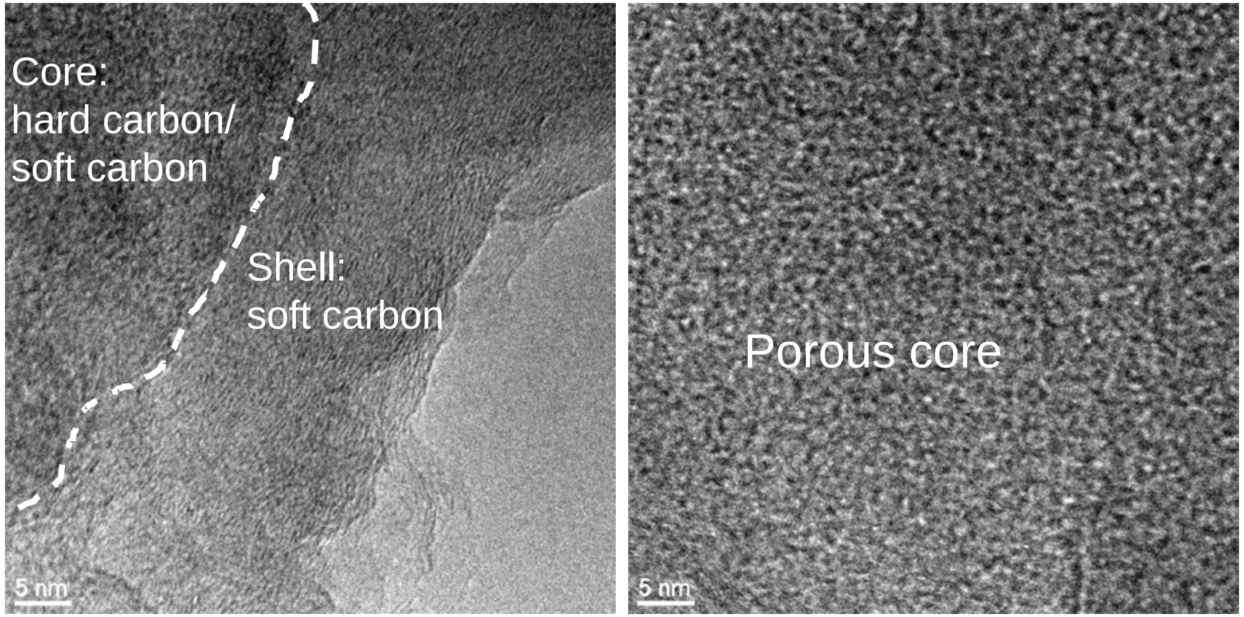
LHCE+$NaBF_4$: NaFSI:NaBF4:TEP:TEGDME:TTE (0.95:0.05:1.3:0.2:2 in molar).

$NaBF_4$ salt additive can further improve cycling stability of cathode.

Technical Accomplishments

4. Development of High-Capacity Carbon Anode

Dual Carbon Structure



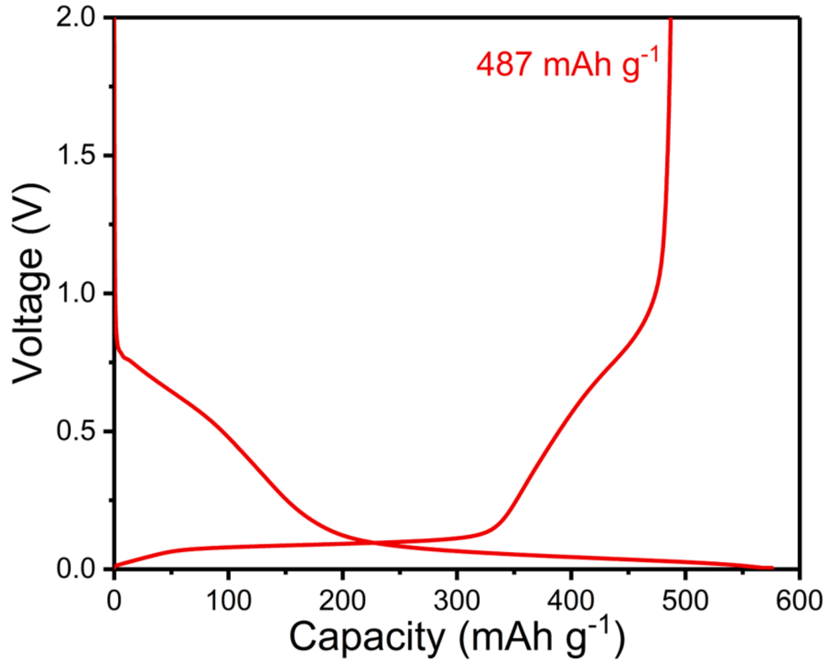
- Soft/hard carbon composite with soft carbon shell and porous soft/hard carbon core.
- Low surface area < 10 m^2 g^{-1}.
- High sealed porosity (~34% based on helium true density of 1.48 g cc^{-1}).

Yi and Zhang, U.S. patent filed

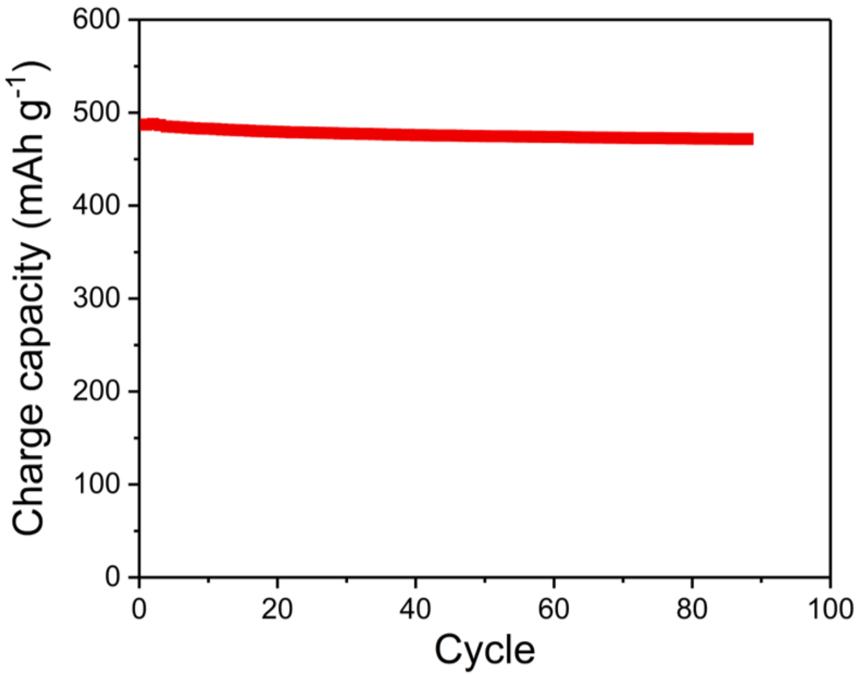
Technical Accomplishments

Electrochemical Performance of Novel Carbon Anode

Initial voltage profiles



Cycling stability



Na||HC half cell

HC electrode: HC:PAA:CB=90:5:5, mass loading: 1–2 mg/cm^2.

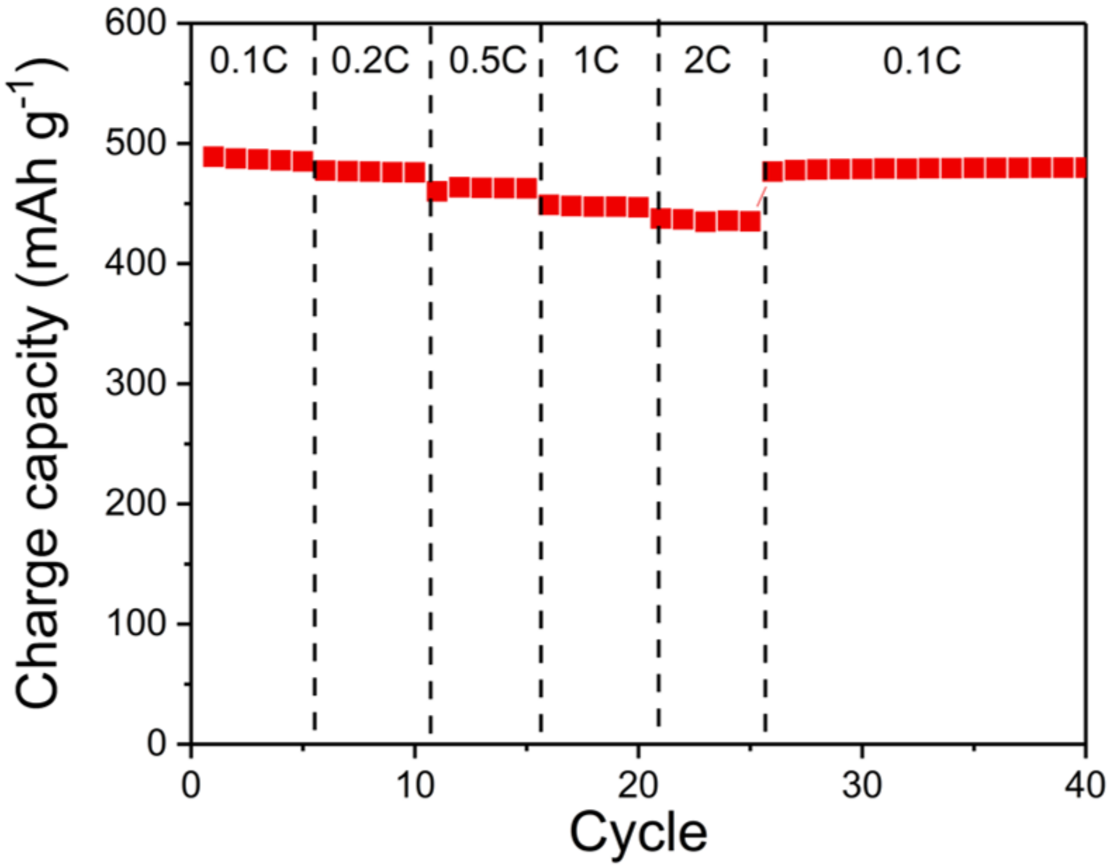
Ely: 1 M $NaPF_6$/EC+DMC (1:1 in weight).

- A record de-sodiation capacity of 487 mAh g^{-1} at 0.1 C (1 C = 450 mA g^{-1}).
- Stable cycling performance with 97% capacity retention after 80 cycles.

Yi and Zhang, U.S. patent filed

Technical Accomplishments

High Rate Capability of Novel Carbon Anode



Na||HC Half cell

HC electrode: HC:PAA:CB=90:5:5, mass loading: 1–2 mg/cm^2.

Ely: 1 M $NaPF_6$/EC+DMC (1:1 in weight).

Excellent high-rate performance: de-sodiation capacity is 435 mAh g^{-1} at 2 C (900 mA g^{-1}).

Critical Assumptions and Issues

- Na-ion battery technology will be a competitive alternative for electric vehicles.
  - The crustal abundance of sodium is far greater than that of lithium; Sodium supply is sustainable with low cost.
- State-of-the-art anode material for Na-ion batteries
  - Hard carbon could be the #1 choice for state-of-the-art anode at the current stage due to safety, cost, and reliability advantages.
  - This project uses hard carbon as the anode to evaluate the electrolyte.
- State-of-the-art cathode for Na-ion batteries
  - Co-free cathode with Earth-abundant elements such as Fe and Mn could further reduce battery cost.

Collaboration and Coordination

- Dr. Chongmin Wang (PNNL) for TEM and STEM images, etc.
- Dr. Mark Engelhard (PNNL) for XPS analysis.
- Dr. Patrick El-Khoury (PNNL) for Raman analysis.
- Dr. Kee Sung Han (PNNL) for NMR analysis.
- Prof. Yong-Sheng Hu (Institute of Physics, Chinese Academy of Sciences) for providing Na-ion cathode material electrodes.

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Remaining Challenges and Future Work

Key Challenges

- The poor wetting problems of Na-ion electrolyte with conventional PP/PE separator.
- Low initial coulombic efficiency of hard carbon anode.
- The compatibility of electrolytes for high-voltage cathode and anode.

Future Work

- Find advanced electrolyte solvent for better wetting with conventional polymer separator.
- Optimized hard carbon structure for higher initial coulombic efficiency and capacity.
- Optimize electrolyte cosolvent/additives to tailor the solvation structures to improve high-voltage and full cell electrochemical performance.

Any proposed future work is subject to change based on funding levels.

Summary

- $NaPF_6/NaBF_4$ in an ether-based electrolyte is stable for Na metal with 99.9% CE and long cycling stability for more than 1000 cycles.

- Nonflammable phosphate-based electrolytes show high compatibility with layered O3-$NaCu_{1/9}Ni_{2/9}Fe_{1/3}Mn_{1/3}O_2$ cathode with the first cycle CE improved from 77% to 98%; stable with hard carbon anode with capacity retention of 94.8% after 500 cycles.

- Effective electrolyte additive: VC in carbonate and $NaBF_4$ in phosphate.

- Novel dual structured carbon anode demonstrates a record capacity of 487 mAh g^{-1}.

Acknowledgements

- Support form DOE/VTO/BMR program is greatly appreciated.

- Team members: Phung M Le, Thanh D Vo, Yan Jin, Ran Yi